Structural Analysis of Coating Film with Ultra-Small-Angle X-ray Scattering

Iwao Soga—Mitsubishi Chemical Corporation*
Hideki Matsuoka—Kyoto University†

The structure of magnetic coating films was analyzed by the ultra-small-angle X-ray scattering (USAXS) technique. Small-angle X-ray scattering (SAXS) has been used to investigate the size, shape, and correlation of the nm sized structure. USAXS, with a measurable range extending to the μm order, can be used to analyze the submicron sized structure of paints and coating films. Preliminary USAXS experiments for a magnetic paint and magnetic coating films revealed that USAXS is useful to evaluate the structure of the particles in the paint and the films. Combined with other experimental methods, USAXS will provide a new kind of information about the structural analysis.

INTRODUCTION

In many applications, product quality is largely affected by the structure of the powder or pigment particles in paints and coating films. The correlation between the particles, which is acknowledged as the dispersion of the powder, is related to the viscosity, stability, flow, mechanical strength, and properties of the products. The shape and size of the particles, which may be affected by the milling process, is not a negligible factor in many cases.

Many methods have been developed to evaluate the structure of paints and coating films.[1-5] Some of the methods observe the structure itself directly. Various types of microscopes are widely used to examine the film structure. Porosity determination of the coating film is a valuable method. Indirect methods measure various properties of paints and coating films and evaluate the structure through the results thus obtained. Mechanical, optical, electrical, and other techniques are often used depending on the sample. For example, stress-strain analysis and dynamic viscoelasticity have been well established and acknowledged as good techniques to evaluate film structure.[3-5] These methods are currently used to observe the structures, but do not always satisfy the requirements. The number of direct methods is limited, and cannot always be applied to the samples by the limitation of materials, substrates, solvents, thickness, size, and volume. The indirect methods are well refined for each application. However, they provide more information than the structures, so they may not reflect the structural differences. Thus total understanding requires continuing effort.

X-ray has a strong transmission capability and has been widely used for the structural analysis. Small-angle X-ray scattering (SAXS) is a powerful technique for the structural analysis of fibers, liquid crystals, polymers, and proteins.[6-8] It can evaluate the size, shape, and correlation in nm order structures. SAXS is a nondestructive method and can be applied to even soft materials such as liquids and suspensions. The information about the microstructure is not local but global since it is collected from the X-ray spot size volume (mm order), and does not come from a limited cross section like a microscope observation. Though SAXS is a powerful tool for structural analysis, it has not been applied for paints and coating films. The measurable range of SAXS is at most hundreds of nm and does not cover the larger size region of interest to the coating industry. Ultra-small-angle X-ray scattering (USAXS) is specially designed to make use of collimated X-rays. With this monochromatized and parallel X-ray, USAXS can measure up to several μm.[8-11] Thus, USAXS can be used for the structural analysis of paints and coating films, and analytical techniques developed for SAXS can be applied. Because the scattering originates from variations in density in the sample, the analysis by USAXS (SAXS) can be applied to various powder-binder mixed systems. In the case of inorganic powders, the specific density is generally very different from that of the organic binders, so a strong and clear scattering pattern suitable for the analysis can be expected.

*Yokohama Research Center, 1000 Kamoshida, Aoba-ku, Yokohama, 227-8502, Japan.
†Department of Polymer Chemistry, Kyoto, 606-8501, Japan.

We report the preliminary results of USAXS experiments for a magnetic paint and magnetic coating films. The dispersion of the magnetic powder for magnetic recording media is one of the most difficult dispersion systems. Still the dispersion of the powder is directly related to the recording performance and media durability. Hence, they have been evaluated by various methods.[5,12-18] In most cases, the dispersion was evaluated through indirect methods such as mechanical properties, magnetic properties, and recording performance. The direct methods are limited because of the high load of the powder, thin film thickness, and small particle size. USAXS can provide direct information about powder structures in the magnetic powder dispersion system.

EXPERIMENTAL

Materials and Samples

All materials were commercial grade samples produced for real production. Acicular Co-γ-Fe_2O_3 (CoFe, length: ~0.3 μm, aspect ratio: 6~10, SSA: 26.7 m^2/g) and platelet barium-ferrite (BaFe, width: ~0.05 μm, aspect ratio: ~3, SSA: 32 m^2/g) were used. For BaFe, strong stacking behavior was reported,[18] so its shape may have less anisotropy than platelets. The binder polymer used was sulfuric salt functionalized poly(vinyl chloride) (PVC). Methyl ethyl ketone (MEK) was used as a solvent. To reduce the complexity of the analysis, the formulation was simplified to a powder-binder-solvent system. The pigment binder ratio (P/B) was varied for some samples and they are listed in *Table* 1.

Magnetic paints were prepared by sand milling. The magnetic particle and the binder solution were mixed in a stainless vessel and dispersed in the presence of ZrO_2 beads for four hours at a solid content (SC) of 55 wt%. Then the pastes were diluted with the solvent to SC=35 wt% and dispersed for 30 min. Coating films were made by applying the paints on poly(ethylene terephthalate) (PET) film with die coating. Thickness was controlled at 2~3 μm. All films were treated with magnetic randomization to attain in-plane homogeneity. Some of the films using the acicular powder were longitudinally oriented with the magnetic field after the randomization. Magnetic properties of the coating films such as saturated magnetic flux density (B_m), residual magnetic flux density (B_r), squareness ($S_q=B_r/B_m$) and orientation ratio (OR=S_q (longitudinal)/S_q (transverse)) were measured with a vibration sample magnetometer (VSM). Porosity of the coating films was determined from the ratio of the measured B_m and calculated B_m.[14] The properties of the films are summarized in *Table* 1.

USAXS Measurement

USAXS measurement was done with Bonse-Hert type scattering equipment[8,9] constructed at Kyoto University. It has two grooved silicon single crystals to obtain the collimated and monochromized X-ray (λ=1.5406 Å). Detailed description of the system was explained in the references.[10,11] Ten pieces of coating film were stacked to adjust the scattering intensity and were placed directly at the beam position. Film planes were set perpendicularly against the incident X-ray. Oriented films were measured in two directions: the orientational direction parallel to the scattering plane (parallel) and the orientational direction vertical to the scattering plane (vertical). The paint without further treatment was measured in a capillary glass tube. The glass tube was completely sealed by glue to prevent the solvent from evaporating during the scanning period. The scattering intensity could be adjusted to select the proper diameter glass tube.

RESULTS AND DISCUSSION

Scattering from the Coating Films

The USAXS patterns of the coating films were examined. In *Figure* 1, the scattering intensity (log scale) from coating film A with the PET base film is plotted against the scattering angle (2θ). For comparison, the scattering from the PET film is also shown. Strong scattering was observed from 2θ=20 to 1,000 sec. The scattering from the PET film was observed only in the center region near the direct beam. Beyond 2θ=200 sec, the scattering from the PET film was negligible, thus the obtained scattering apparently originated from the coating film. From 20 to 200 sec, the scattering from the coating film was evaluated to subtract the contribution from the PET film. At larger angle regions, the scattering intensity became close to the noise level at 2,000 sec. Hence the scattering pattern of the coating film could be measurable from 20 to 2,000 sec. This roughly corresponds to the size scale of 160 Å to 1.5 μm. No typical pattern originating from 2~3 μm (coating film) or 10 μm (base film) object was observed from the 20 to 3,000 sec region. So the scattering from the layer structures will be limited in the center region. Because the intensity ratio of the direct beam and the scattered X-ray was more than

Table 1—Properties of the Coating Films

Film	Powder	Orientation	Press	P/B (vol%)	BM (mT)	Porosity (vol%)	S_q	OR
A	Platelet	No	Yes	64	175	32	0.50	—
B	Platelet	No	No	64	159	38	0.50	—
C	Platelet	No	No	52	151	27	0.49	—
D	Acicular	Yes	Yes	58	213	27	0.89	2.8
E	Acicular	Yes	No	58	198	32	0.89	2.9
F	Acicular	No	No	58	187	36	0.67	—
G	Acicular	No	No	52	162	39	0.49	—

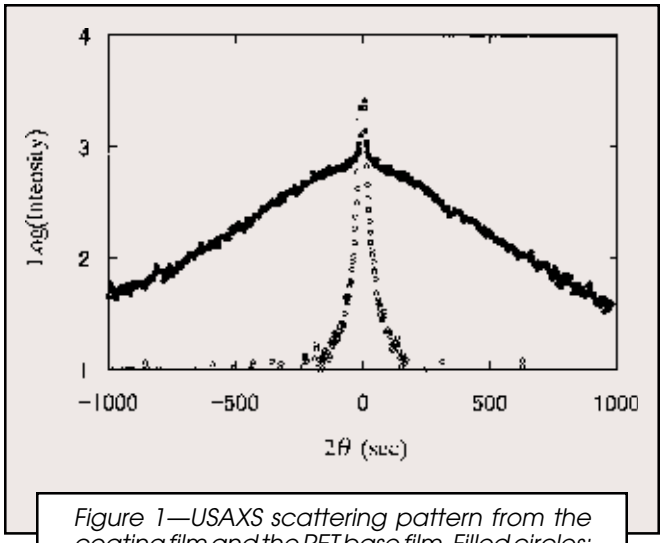

Figure 1—USAXS scattering pattern from the coating film and the PET base film. Filled circles: Film A with PET base film, Open circles: PET Film.

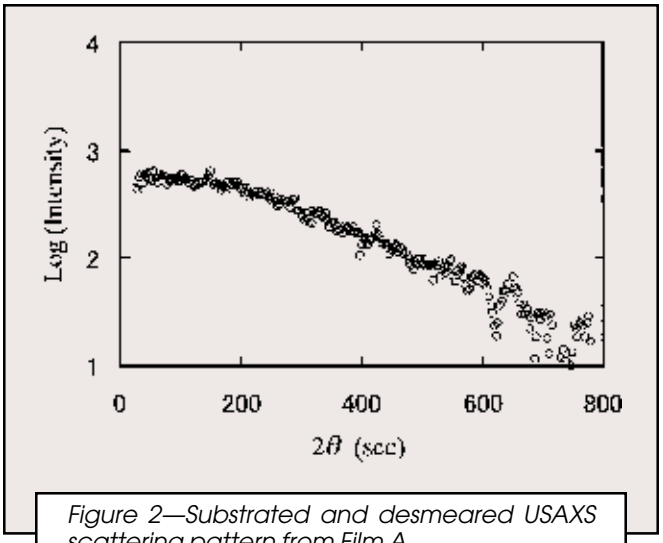

Figure 2—Substrated and desmeared USAXS scattering pattern from Film A.

10^3, a multiple scattering can be negligible. From these results, it appears that USAXS has range wide enough for analyzing the structure of the magnetic coating film.

To analyze the scattering patterns, the following points should be considered. The scattering is based on the difference of the electron density in the sample materials. Hence, even the pore can be the source of scattering. To interpret the scattering pattern precisely, it is necessary to combine other experimental results and/or information based on the formulation. For the magnetic coating films in these experiments, the specific densities of the magnetic powder, the binder, and the pores were at a ratio of 5.5 : 1.2 : 0, respectively. Because the scattering intensity is proportional to the square of the density difference, the contrast is much larger for the magnetic powders against the other two. Hence, we assumed that the scattering pattern mainly originated from the structure of the magnetic powders. For more precise analysis in which the density difference between the pores and the binder is not negligible, the scattering from the pores can be eliminated by introducing a liquid of suitable density. This treatment will also be preferable for a system using lower specific density powder. Because of the low contrast, such a system should be analyzed as a powder-binder-pore system. However, it is effectively reduced to a two-component system by the liquid immersion.

Secondly, in principle, information for both the particle shape and the particle correlation are included in the scattering curve. The information on smaller scales appears at larger angles and that on larger scales at smaller angles. When the distance between the particles is substantially larger than the particle size (e.g., for dilute solutions), only the particle shape will be detected. When the particles are densely packed, the scattering pattern will include the particle correlation information. If the size scale is similar, both may be evaluated from one scattering pattern, but the scattering pattern needs to be analyzed carefully. The source of the scattering should be determined by the comparison with other experimental results and/or by fitting the curve by the scattering formula for model particle scattering and model correlation function.

Figure 2 shows the corrected scattering pattern of coating film A. The base film intensity was subtracted and the scattering pattern was desmeared to correct the slit configuration.[6] All scattering patterns discussed below (see also *Table* 2) are similarly treated; subtracting the base film scattering in the corresponding setting; desmearing the curve for the data range from the center to closing to the noise level. *Figure* 2 seems to show a maximum around 50-100 sec. If the structure is completely regular, the peak angle is the Bragg's angle as can been seen for crystalline materials. Even amorphous samples show a broad maximum angle corresponding to the nearest neighbor correlation, but the maximum of *Figure* 2, if it exists, is too broad and vague. It is not feasible to conclude whether this maximum reflects the film structure or not.

For an acicular-shape powder, the scattering behavior is rather different. Three scattering patterns from two films consisting of the acicular powder are shown in *Figure* 3. Two are from the oriented film (film D), but different scattering directions (vertical and parallel direction). The rest is from the randomized film (film F). It is clear that the scattering patterns are different, reflecting the structural

Table 2—USAXS Results of the Coating Films

Film	Powder	Orientation	Scattering Direction	Peak Angle (2θ) (sec)	Correlation Length (*lc*) (nm)
A	Platelet	No	—	50-100	13.7
B	Platelet	No	—	N/A	13.4
C	Platelet	No	—	N/A	18.2
D	Needle	Yes	Parallel	N/A	21.0
D	Needle	Yes	Vertical	~220	N/A
E	Needle	Yes	Parallel	N/A	21.4
E	Needle	Yes	Vertical	~200	N/A
F	Needle	No	—	N/A	18.5
G	Needle	No	—	N/A	24.5

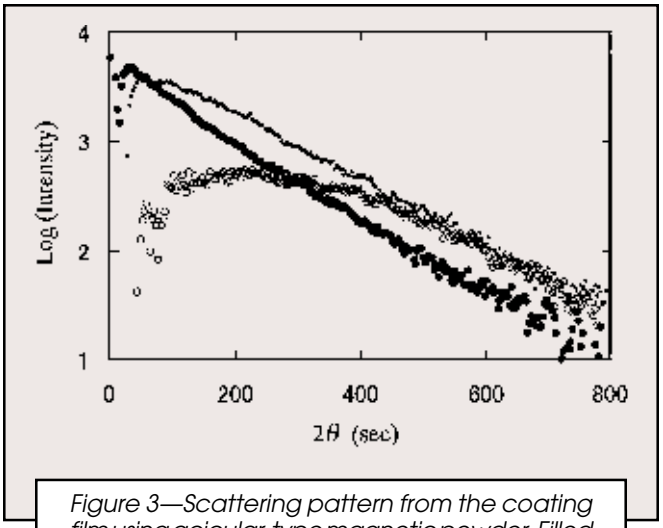

Figure 3—Scattering pattern from the coating film using acicular-type magnetic powder. Filled circles: oriented film (film D)-parallel direction. Open circles: oriented film (film D)-vertical direction. Dots: randomized film (film F).

difference of each film. It is also clear that the scattering pattern largely depends on the degree of the randomness and the direction of the orientation. In the case of the vertical setting of the oriented film, there is a broad maximum around 200 sec and it is clearer than that of film A. With this configuration, the acicular powder tends to align vertically against the scattering direction. For an elongated fibril, the alignment is more strong and regular, and the specific peak corresponding to the fiber distance can be observed. In the case of the magnetic powder, the length is limited, the alignment is imperfect, and the correlation is more random, so the peak is broad. However, at least this means that the structure of film D is more organized than film A. Much more organized samples will give a clearer peak and meaningful analysis will be possible.

Structure of the Coating Films

For detailed analysis of the film structure, analytical methods must be applied. Guinier analysis,[6] which gives the size information of the particles, did not fit well with these scattering patterns from the coating films. Guinier analysis is based on the scattering from an independent isolated object. Dilute solutions or coating films with low P/B ratio are suitable cases. Since the structure of the magnetic coating film is considered to be rather continuous and random, Guinier analysis is not a suitable method. To analyze these types of materials, Debye analysis is more suitable.[19,20] This method was originally introduced to analyze a bicontinuous random phase, and a statistical parameter expressing the randomness was introduced. In Debye analysis, scattering intensity (I) is expressed by,

$$I = K/(1 + q^2 \times l_c^2)^2 \quad (1)$$

where l_c is the correlation length, K is a constant, and q is a scattering vector calculated from,

$$q = 4 \times \pi \times \lambda^{-1} \times \sin\theta \quad (2)$$

Here λ is the wavelength of the X-ray. By plotting $I^{-1/2}$ against q^2, l_c is calculated from the slope and the intercept of the fitted straight line. *Figure* 4 shows the Debye plot of the scattering pattern of film A. Data points are well fitted with the straight line, and l_c thus obtained is 13.7 nm. The correlation length is a statistical value of the structure and is considered to relate with the distance between the particles in the magnetic films. The size of the BaFe particle is roughly ~50 nm in diameter and ~17 nm in thickness with the platelet shape. From VSM results, the volume fraction of the powder in the film is 44.1 vol% for film A. If the particles in the film are arranged regularly and isolated, the particle spacing becomes 31% of the particle size. This means the particle distance of ~15 nm for the diameter direction and ~5 nm for the thickness direction. Because the packing of the powder is more random and inhomogeneous and there is stacking of the particles, this estimation will not be precise. However, we can confirm that the value of 13.7 nm from Debye analysis is in the reasonable range as a parameter of the particle distance.

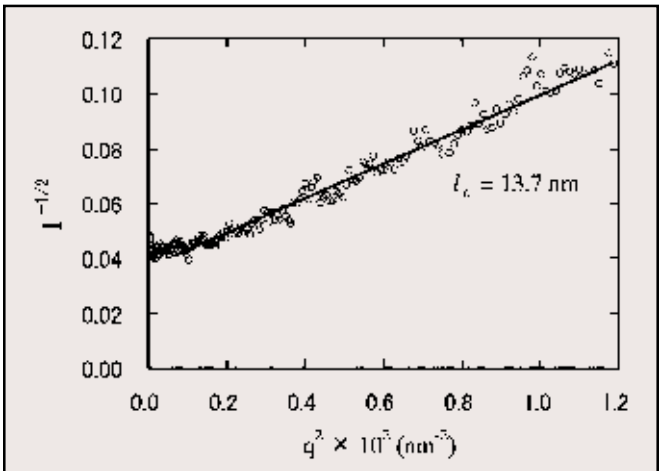

Figure 4—Debye plot of the coating film (film A).

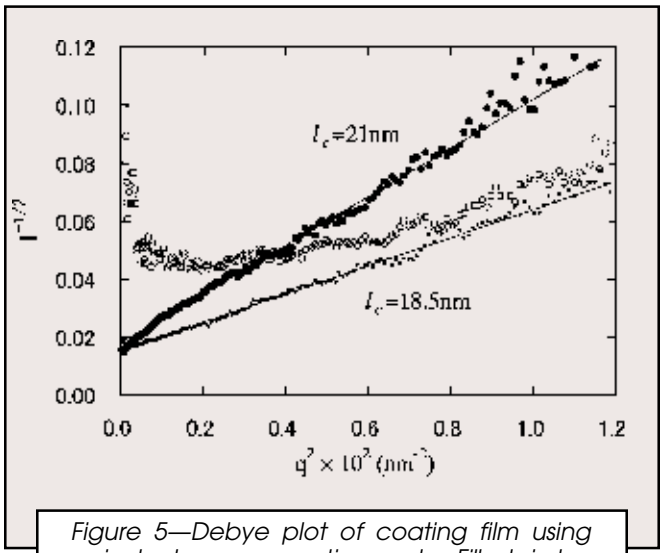

Figure 5—Debye plot of coating film using acicular-type maganetic powder. Filled circles: oriented film (film D)-parallel direction. Open circles: oriented film (film D)-vertical direction. Dots: randomized film (film F).

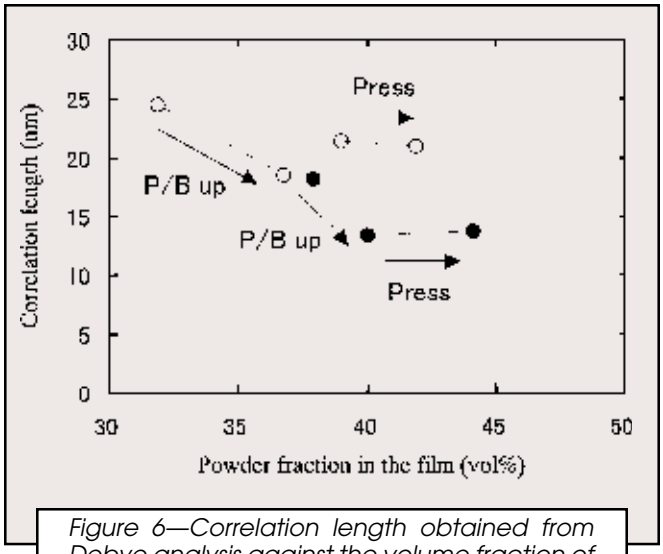

Figure 6—Correlation length obtained from Debye analysis against the volume fraction of the powder of the film. Filled circles: platelet-type particles. Open squares: acicular-type particles.

Figure 5 shows the Debye plots of the acicular powder films. The plot of the vertical setting of film D is not fitted by a straight line. As discussed previously, the rather organized structure for that direction is not suitable for the Debye analysis, which is based on a random-continuous phase. The two other plots show an excellent linearity in this Debye plot and l_c is calculated to be 21 nm for the oriented film and 18.5 nm for the random film. Because the particle size is larger for the acicular powder, it is reasonable that l_c is larger than that in film A. We suppose that the difference between the random and the oriented film, especially for larger l_c for less dense film, is due to the effect of powder contact through the magnetic interaction, although we cannot say so conclusively at this stage.

Figure 6 summarizes the correlation length of the various films as a function of the powder fraction in the film. The volume fraction of the powder generally increases with a P/B ratio within the range of good dispersion. The pressing process also increases the volume fraction. These were confirmed for both the acicular powder and the platelet powder in *Figure* 6. The interesting point is the change of the correlation length. In the case of the increase in the P/B ratio, the increase of the volume fraction accompanied the decrease of the correlation length, while in the case of the pressing process it did not. This can be explained as follows. The correlation length of this scale is considered to reflect mainly the nearest neighbor distance between the particles. When the P/B ratio increases, the binder amount per the particle decreases in the paint and in the coating film. In the paint, this results in fewer adsorbed binder on the particles and decreases the colloid stability. In the film, thinner adsorbed polymer layer leads to the closer distance of the particles. Consequently the correlation length becomes smaller. In the case of the pressing, the increase of the volume fraction is achieved by the crushing of the pores in the film. It is plausible that the pores are not homogeneously distributed in the film; there are various size micro pores between particles, and larger pores between particle clusters. In that case, the larger pores are more easily crushed by the pressure, so the distance between the clusters will be directly affected by the calender process. On the other hand, the decrease of the nearest neighbor distance between the particles will be smaller, because the particles in the clusters are contacted via the adsorbed polymers. Hence, the correlation length reflecting the nearest neighbor distance between the particles tends to be left intact.

The correlation length evaluated by USAXS focuses on the distance between the adjacent particles. This is a new kind of information reflecting the microstructure. Thus, it can compensate for the volume fraction data of the film, which is averaged for the whole film and loses the detailed information of the microstructure. The pore size distribution from a mercury porosimeter or particle percolation from electric conductivity may provide a similar kind of information about the microstructure. Unfortunately, they cannot be applied to current magnetic coating films. Also, since all these methods observe different aspects of the microstructure based on the different principles, USAXS surely extends the range of applicable samples and provides analytical clues. For these reasons, USAXS should be a useful new experimental technique for structure analysis for these systems. By combination with other experimental techniques, the structure of the powder and the pores in the coating film can be understood more precisely. For larger structures, such as the distance between particles clusters, further analysis for a smaller angle region is necessary and it will be possible by USAXS.

Paint Analysis

The scattering measurement was also applied for the paint of film A. The paint was measured in the original form without further treatment such as dilution. Although the paint was completely opaque, USAXS could be applied since X-rays can pass through opaque systems. The detected scattering intensity was strong enough to conduct the analyses. Guinier analysis could be applied. Scattering intensity (I) is expressed by,

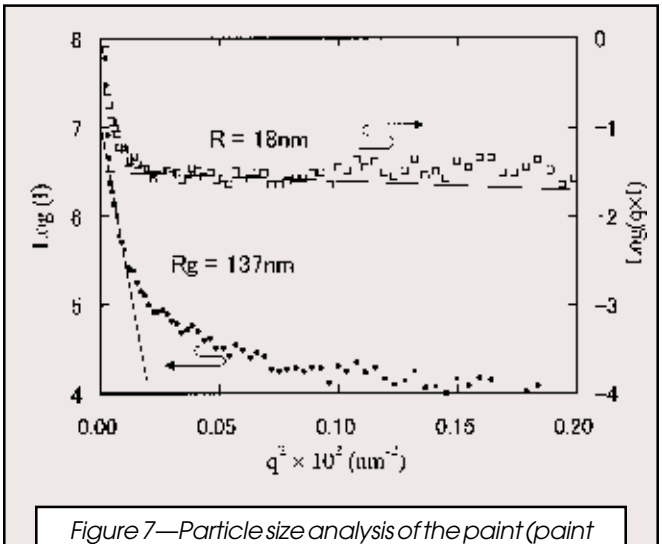

Figure 7—Particle size analysis of the paint (paint of film A). Filled circles: Guinier plot (Log (I)-q^2). Open squares: Log (qxI)-q^2 plot.

$$I = \exp(-q^2 \times R_g^2/3) \quad (3)$$

where R_g is the radius of gyration of the particles. By plotting $\log(I)$ against q^2, R_g can be calculated from the slope of the straight line. *Figure* 7 shows the results of the analysis. Because the particles are acicular, $\log(q \times I)$ analysis, which is often used for size determination of liquid crystals and proteins, was also applied.[21] From the slope of the $\log(q \times I)$-q^2 plot, the radius of the cylinder (R) for needle-type particles was calculated. The length of the particle (H) is related to those two parameters by,

$$R_g^2 = (R^2/2) + (H^2/3) \quad (4)$$

From *Figure* 7, R_g and R are estimated to be 137 nm and 18 nm, respectively. H obtained from equation (4) is 236 nm. Because the particles were rather polydisperse in size, the slopes could not be perfectly fitted by a single straight line. Instead of adapting a multiple Guinier curve, we drew most probable (average) lines in the scattering range of corresponding scale size. The cylinder radius and the length obtained were plausible values compared to the 0.015~0.025 μm radius and the ~0.3 μm length from the catalog value. Still, besides the polydispersity, we suspect the flocculation of the magnetic particles originating from the strong magnetic interaction disturbed the result. Because the Guinier analysis assumes independent particles, this method will be more useful for more weakly interacting colloid particles in lower SC paints.

CONCLUSIONS

USAXS was applied to analyze the structure of magnetic paint and magnetic coating films. With extended scattering angle range, the obtained scattering patterns were sufficient to analyze the coating applications. The scattering patterns from the coating films can be used as an indicator of the degree of the orientation and the orientational direction. Debye analysis of the scattering pattern provided the correlation length of the coating film, which is considered to be related to the nearest neighbor distance of the particles in the film. The correlation length was found to be a useful parameter of the film structure. Combined with other data such as the volume fraction, the structural change against the P/B ratio and the pressing process was understood more precisely. The analysis of the paint showed the feasibility of the size determination of particles in the original dense paint.

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